

Resonant vibrational excitation of CO₂ by electron impact: Nuclear dynamics on the coupled components of the 2Π_u resonance

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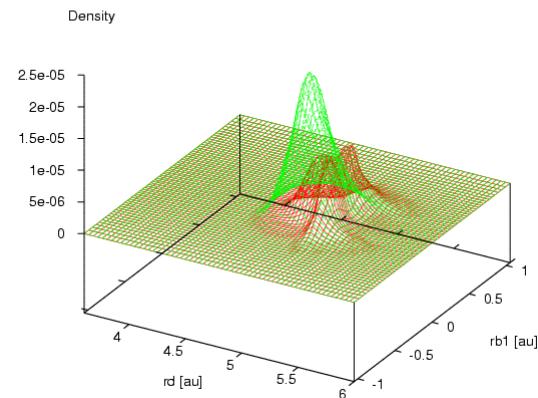
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Time : 20.000
A1 + B1, Start on A1 surface



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Resonant Electron Scattering From CO₂

There is a well-known resonance at ~3.8 eV through which vibrational excitation occurs. The electron attaches in the lowest unoccupied molecular orbital (π_u) to make a $^2\Pi_u$ state of CO₂ -

- New experiments reveal structure in the vibrational excitation cross sections that probes the polyatomic nature of the collision

The problem: from first principles, solve the scattering problem including the nuclear dynamics, predict the cross sections and show how they display the polyatomic dynamics of the collision

Breaking up the problem into two parts:

- (1) Electron scattering for fixed nuclei -- $^2\Pi_u$ symmetry, $\rightarrow ^2A_1$ and 2B_1 upon bending
- (2) Nuclear dynamics during the resonant collision: non-adiabatic coupling of electronic and nuclear motion

An Electron- CO₂ Primer

- CO₂ is linear in equilibrium geometry R_{CO} = 2.1944 a₀
- At the equilibrium geometry of CO₂, CO₂⁻ is an unbound 2Π_u resonance state (~3.8 eV above CO₂)
- The resonance state is doubly degenerate in linear geometry, but the degeneracy is lifted upon bending (Renner-Teller coupled states, 2A₁ and 2B₁)
- A low-energy enhancement in elastic scattering comes from a CO₂⁻ virtual state (confirmed by Morgan in 1998)
- CO₂⁻ is bound in linear geometry for CO bond distances greater than ~2.5 a₀
- CO₂⁻ is bound for R_{CO} = equilibrium value when it is bent by ~25 degrees

Recent
Experi-
ments --
M.
Allan
2002

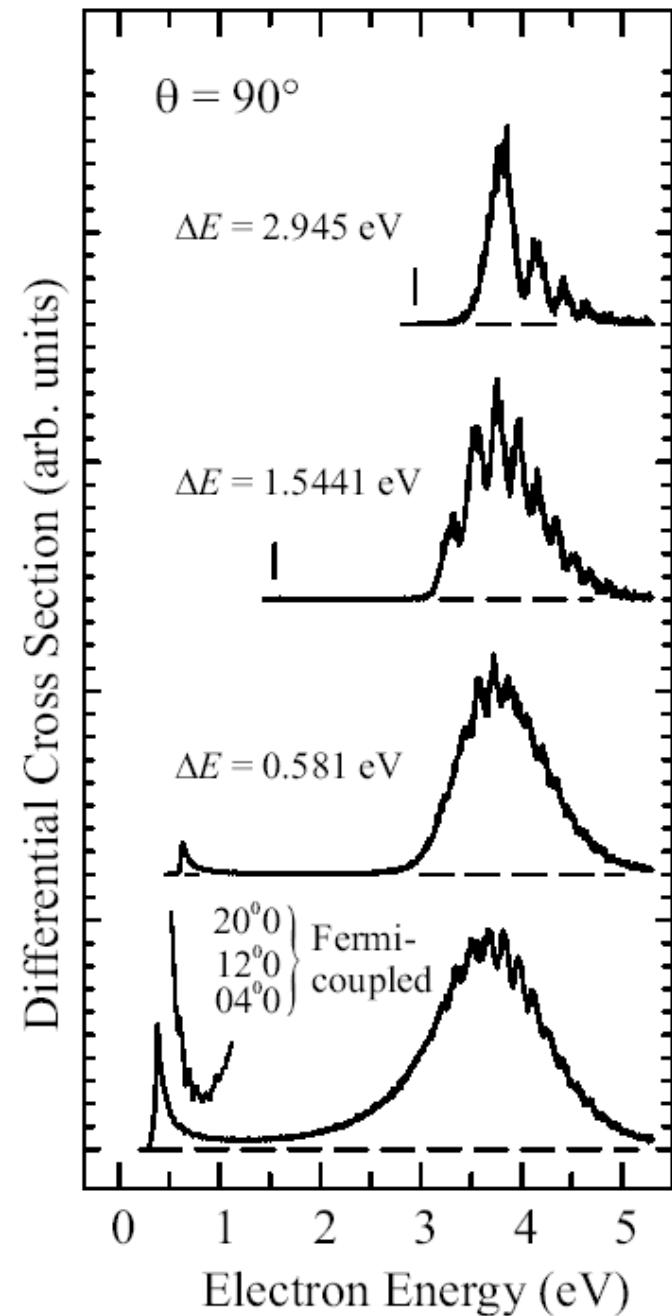
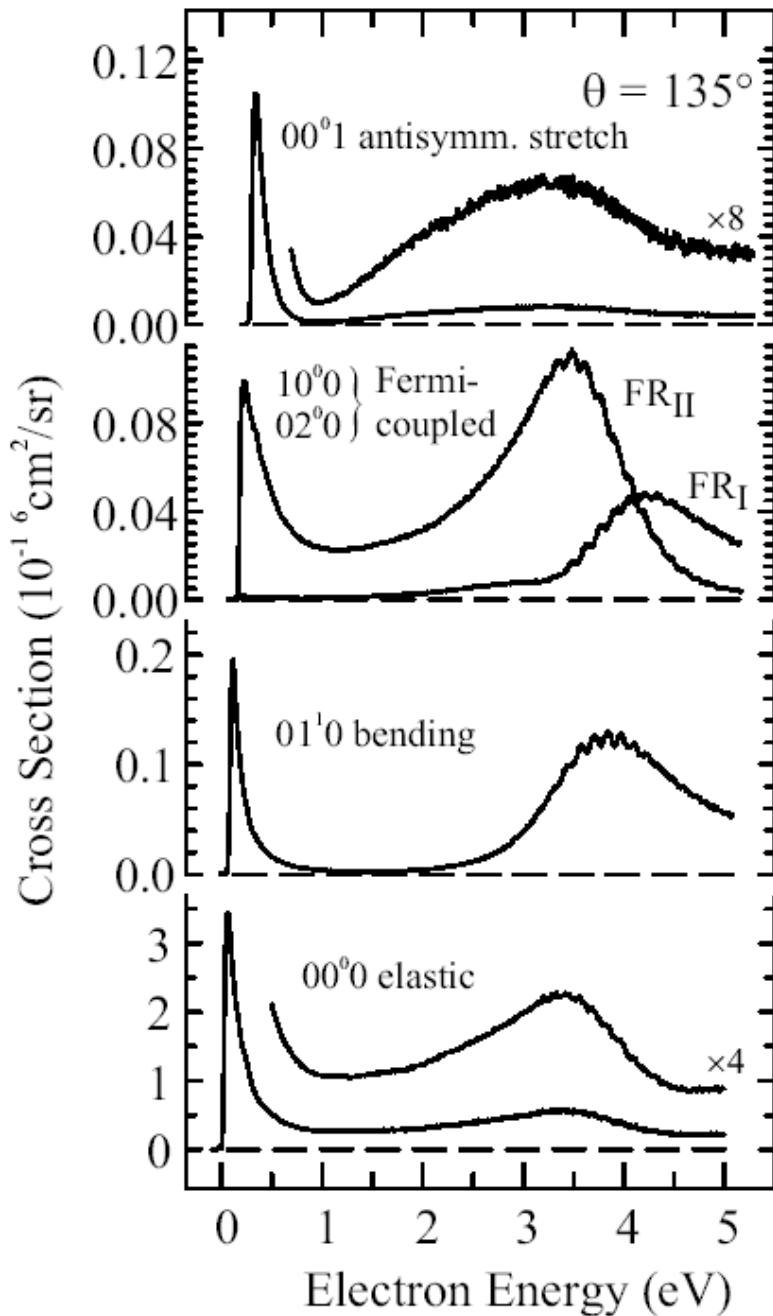


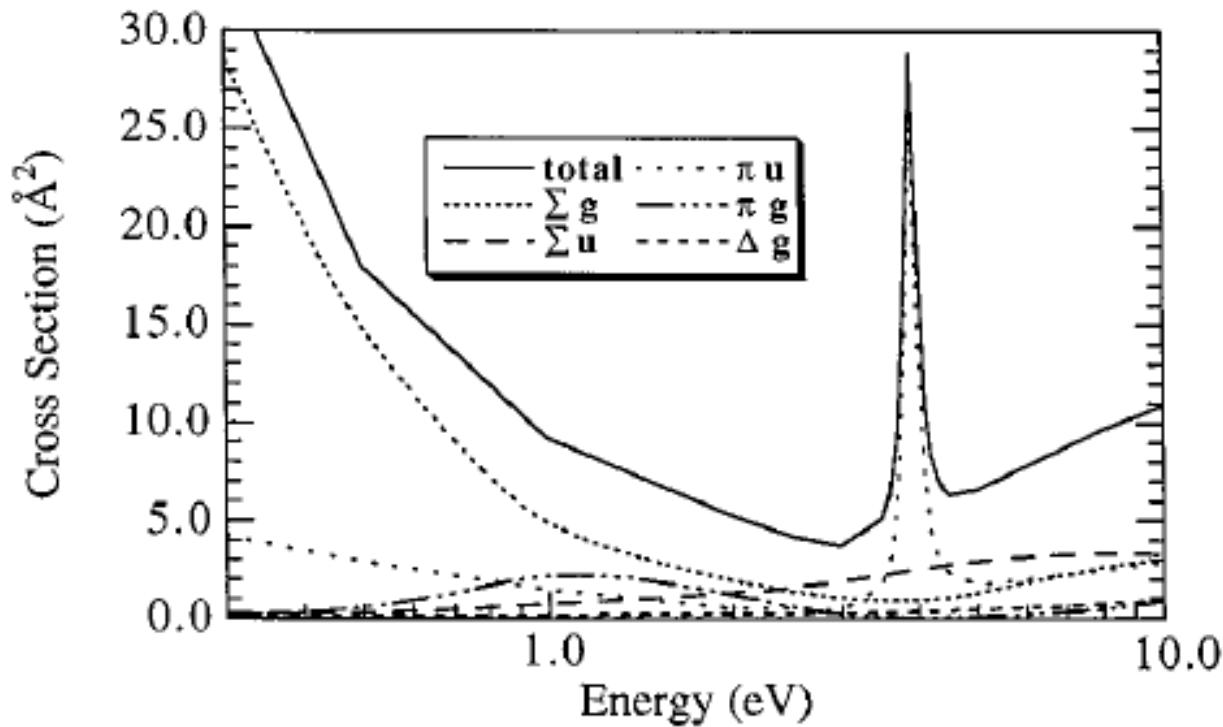
Figure 1. Overview of the elastic and vibrationally inelastic cross sections in CO_2 . Reproduced from Allan (2002).

Computational Electron-Molecule Scattering – the fixed-nuclei electronic problem

- At the low collision energies of interest to EDC, incident electron and target electrons are indistinguishable – electronic *structure* and electron *dynamics* are inseparable.
- The key to a successful approach is the interface between electronic structure and electron dynamics.
- Virtually all successful modern approaches are *variational*.
- Our approach is based on the complex Kohn variational method – a Hamiltonian – based, anomaly-free approach that allows us to fully exploit the rich infrastructure of bound-state quantum chemistry

Electron- CO_2 cross section calculated with fixed nuclei

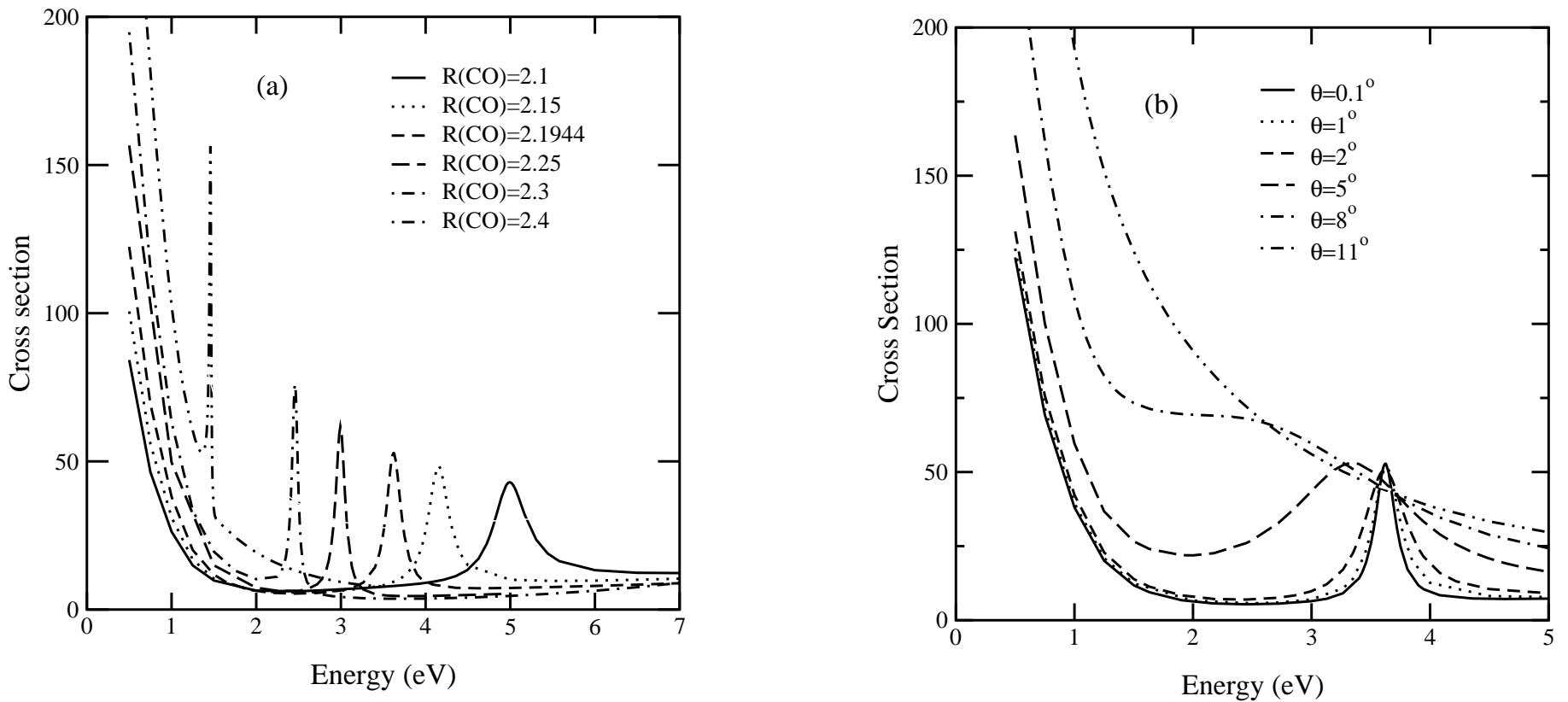
at equilibrium geometry



Threshold enhancement and structureless sharp resonance peak ~ 3.8 eV

Fixed Nuclei Electron-Scattering Cross sections in

$^2\text{A}_1$ symmetry for varying geometries



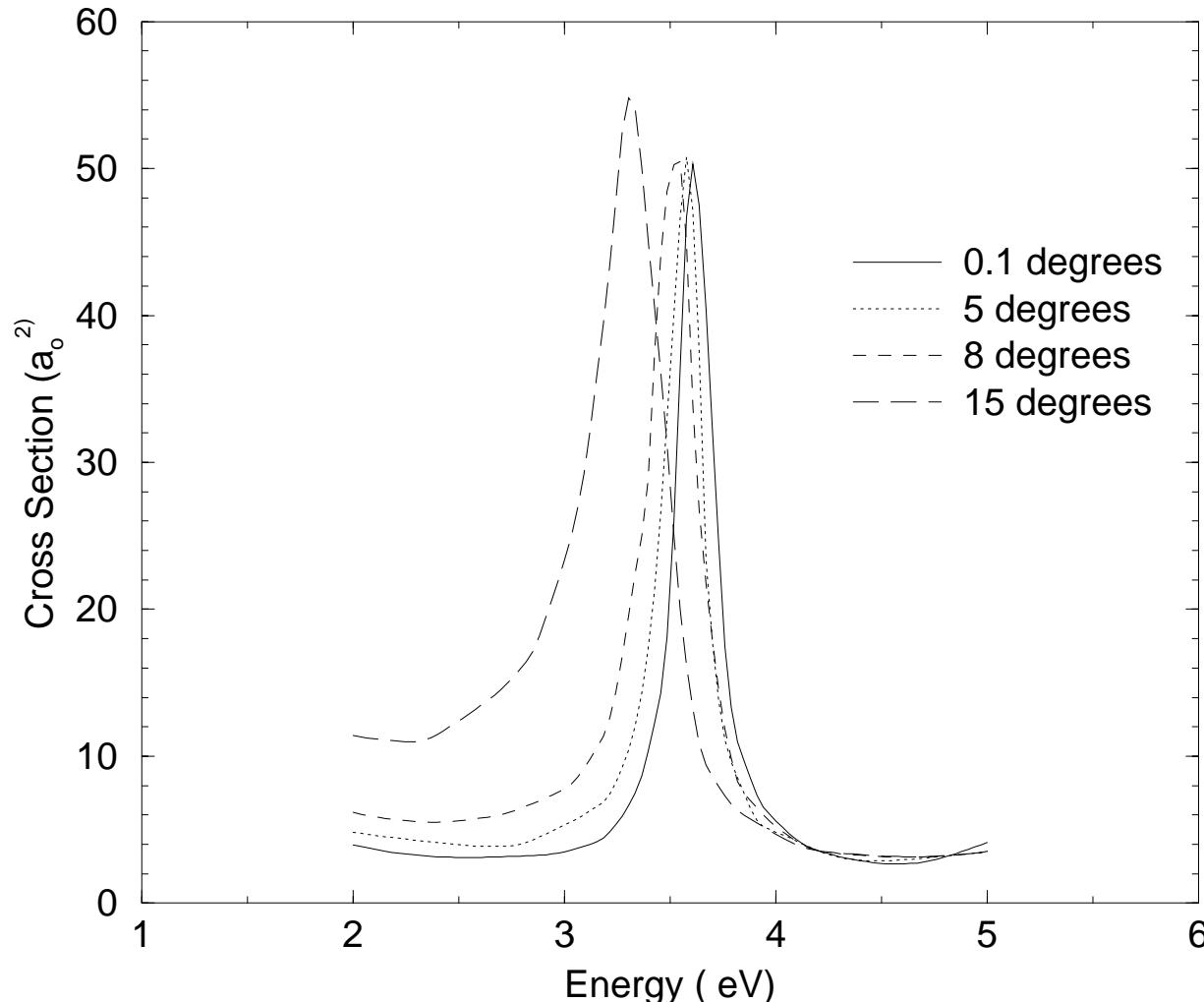
Resonance feature gives a **position and width**: A complex energy for the resonance $E_{res}(R) = E_r - i\Gamma/2$ which can be understood in the simplest interpretation via

$$|\Psi(r, t)|^2 = |\psi(r)e^{-iE_{res}t}|^2 = |\psi(r)|^2 e^{-\Gamma t}$$

Fixed Nuclei Electron-Scattering Cross sections in

$^2\text{B}_1$ symmetry for varying geometries

Fixed–Nuclei Cross Section – B_1

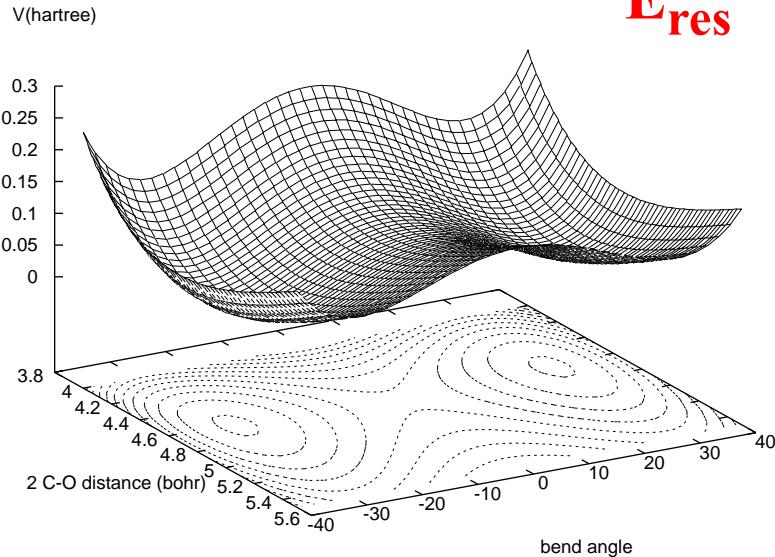


Weaker dependence of width and position on geometry than for $^2\text{A}_1$. Surface almost parallels ground state.

Complex Potential Surfaces for $^2\text{A}_1$ and $^2\text{B}_1$ resonance states

$^2\text{A}_1$

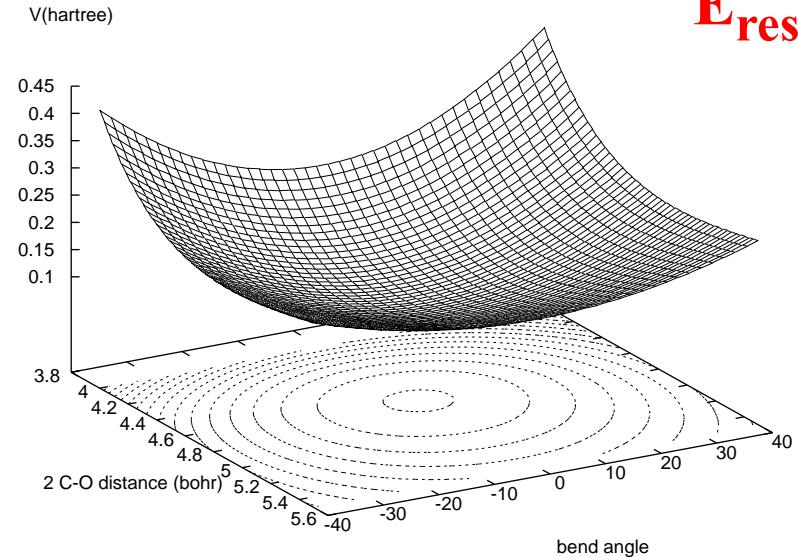
A1 Resonance Ion surface



E_{res}

$^2\text{B}_1$

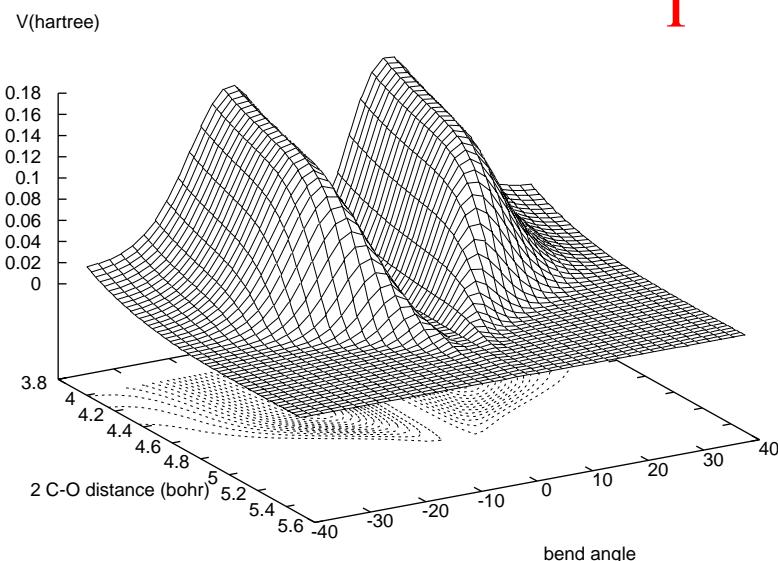
B1 Resonance Ion surface



E_{res}

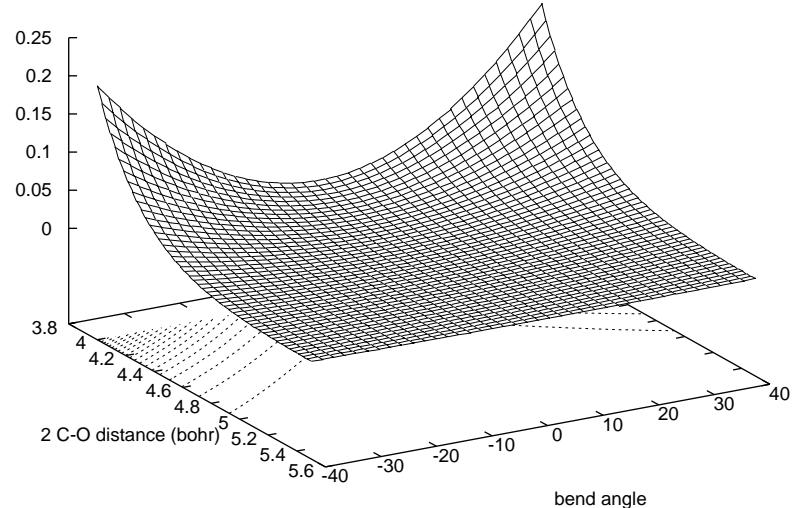
A1 Resonance Width

Γ



B1 Resonance Width

Γ



The Nuclear Dynamics: Formulation of the problem

- Partition the total wave function into resonant and non-resonant components
- For a single, isolated resonance, use Born-Oppenheimer approximation for both resonance and nonresonant background
- The T-matrix (scattering amplitude) for vibrational excitation (or dissociative attachment) is given by the nuclear wave equation

$$[E - E_{res}(R) - K_R] \xi(\mathbf{R}) = \langle \Psi_{res} | H_{el} | P\phi_{v_i}^+ \rangle_{(\mathbf{R})} + \langle \Psi_{res} | H_{el} P G^+ P H_{el} | \Psi_{res} \rangle_{(\mathbf{R})} \xi(\mathbf{R})$$

A series of approximations converts this essentially exact equation into the “Boomerang” or “local complex potential” approximation

Local Complex Potential or “Boomerang” Approximation

Time-independent formulation:

$$\{E - H_{\text{anion}}\} \xi(\mathbf{R}) = \Phi_{\text{initial}}(\mathbf{R})$$

$$\Phi_{\text{initial}}(\mathbf{R}) = \left(\frac{\Gamma(\mathbf{R})}{2\pi} \right)^{1/2} \chi_i(\mathbf{R})$$

Hamiltonian for nuclear motion of anion with local complex potential

$$H_{\text{anion}} = K_R + [E_{\text{res}}(\mathbf{R}) - i\Gamma(\mathbf{R})/2]$$

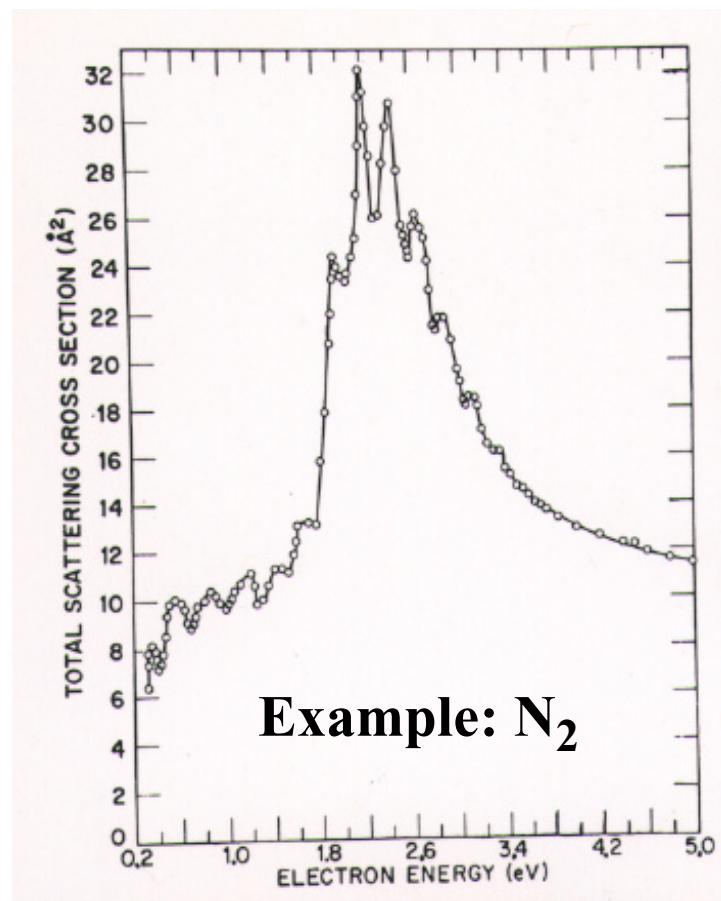
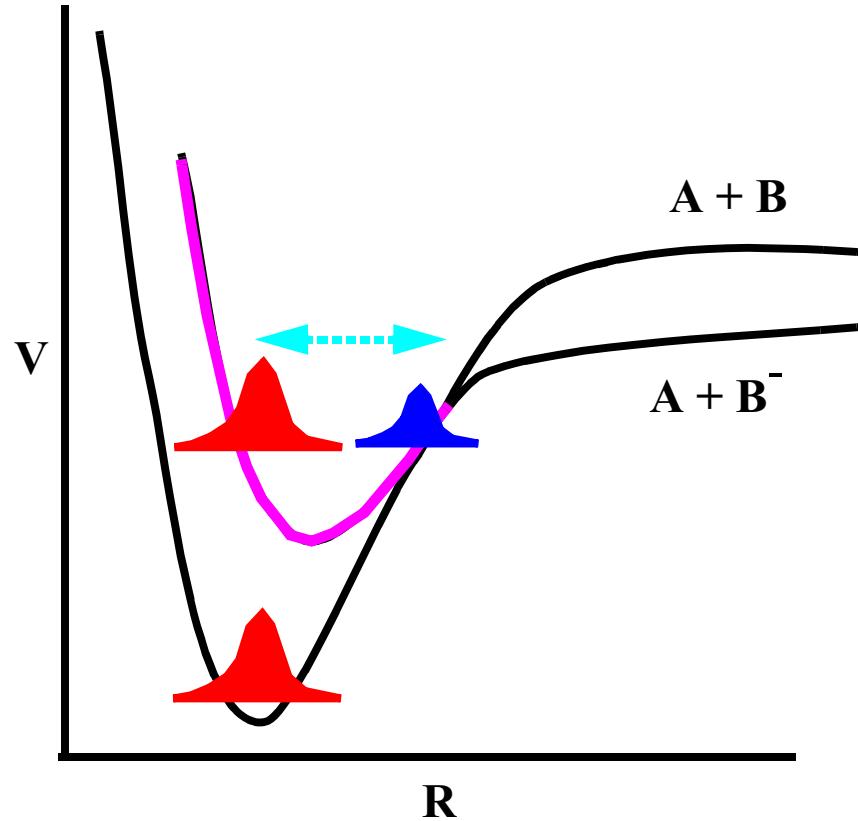
 Local complex potential

Scattering amplitude and cross section:

$$T_{f,i}(E) = \langle \Phi_{\text{final}} | \frac{1}{E - H_{\text{anion}}} | \Phi_{\text{initial}} \rangle$$

$$\sigma_{f,i}(E) = \frac{4\pi^3}{k^2} |T_{f,i}(E)|^2$$

Local Complex Potential or “Boomerang” model for Resonant Vibrational Excitation in 1D (diatomics)



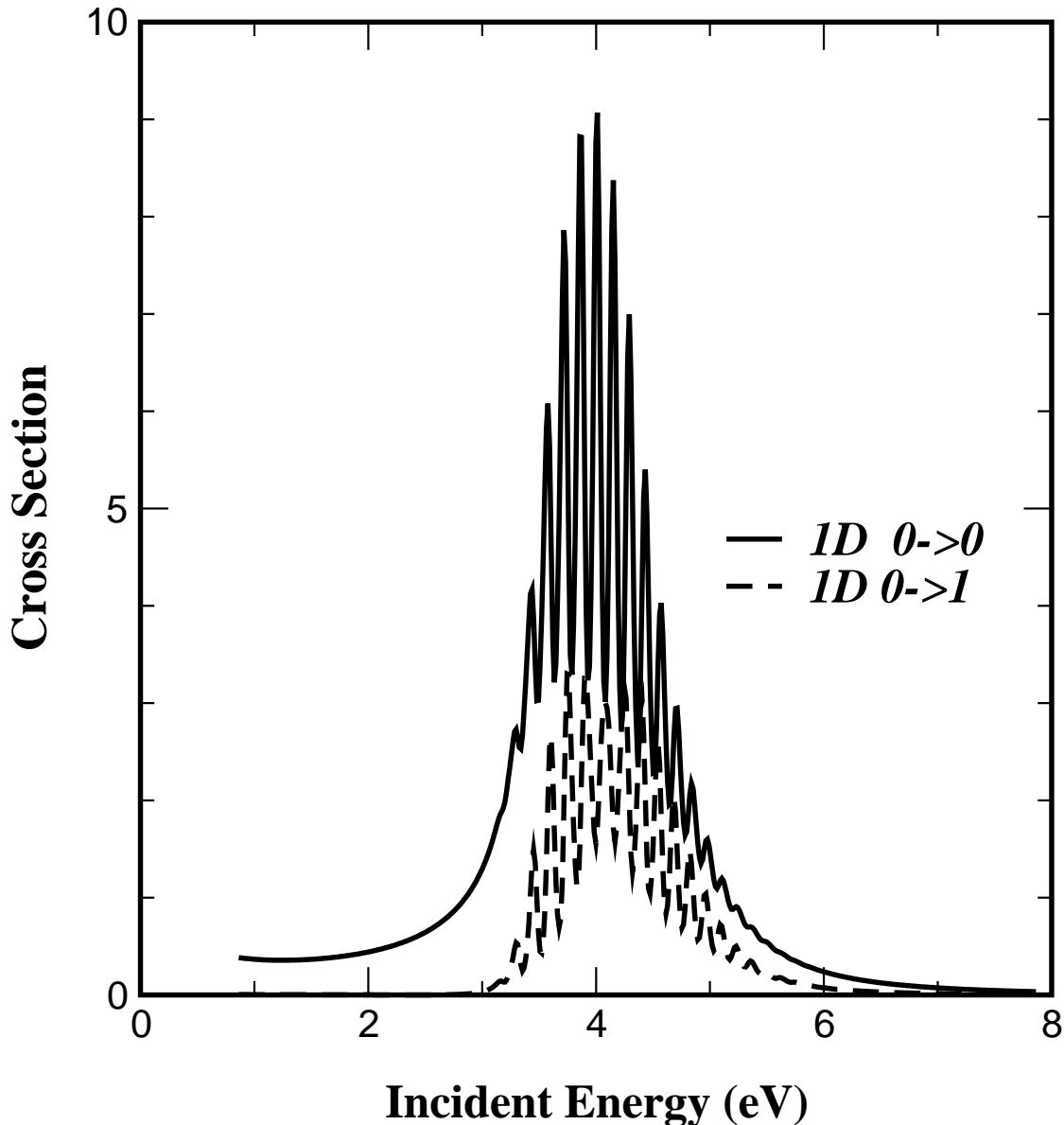
Time-dependent formulation $\Phi_{initial}(R) = \left(\frac{\Gamma(R)}{2\pi} \right)^{1/2} \chi_i(R)$

$$T_{f,i}(E) = -i \int_0^{\infty} e^{iEt} \langle \Phi_{final} | \Psi_t \rangle dt$$

with

$$\Psi_t = e^{-iH_{anion}t} |\Phi_{initial}\rangle$$

A one-dimensional treatment of CO₂ using just the ²A₁ component of the resonance?

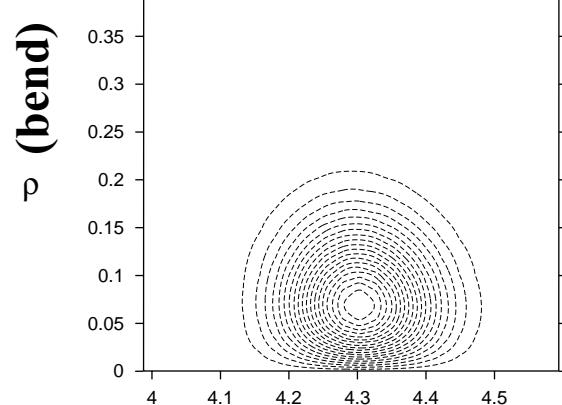


Structure entirely *unlike* experiment!

Also, single excitation in
only symmetric stretch is
not a physical state of CO₂!

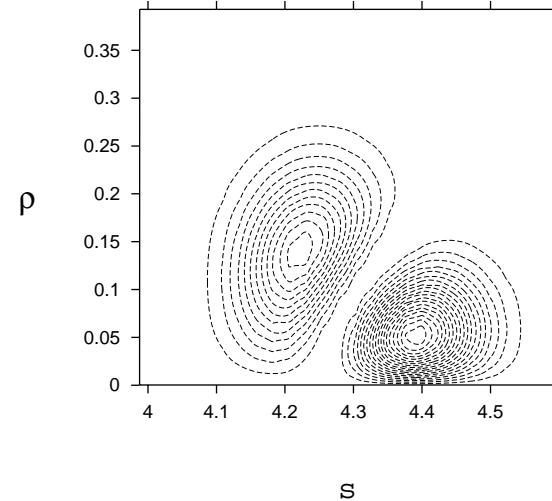
Vibrational states of CO₂ -- Near degeneracy of $\nu_{\text{stretch}} \sim 2\nu_{\text{bend}}$

(0,0,0)

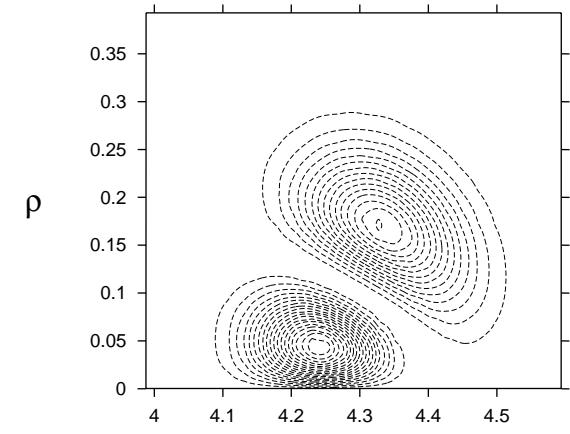


s (stretch)

Fermi dyad {coupled $(1,0^0,0)/(0,2^0,0)$ }

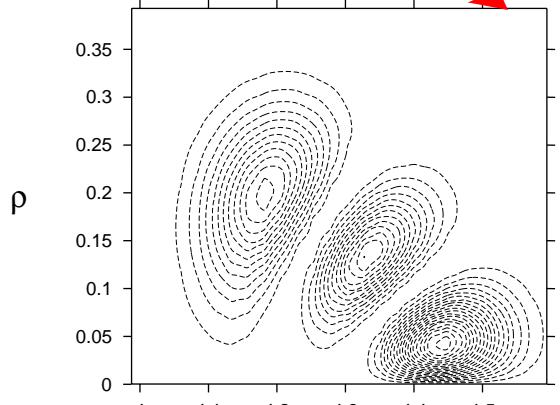


s

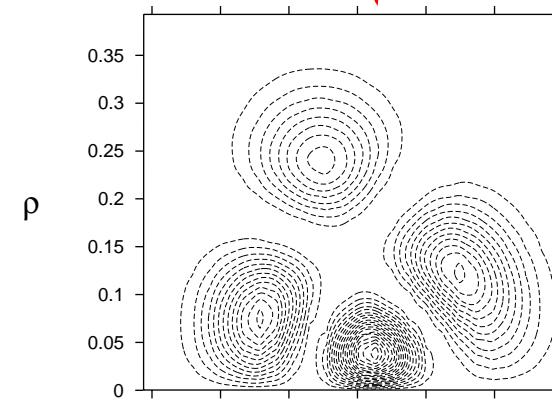


s

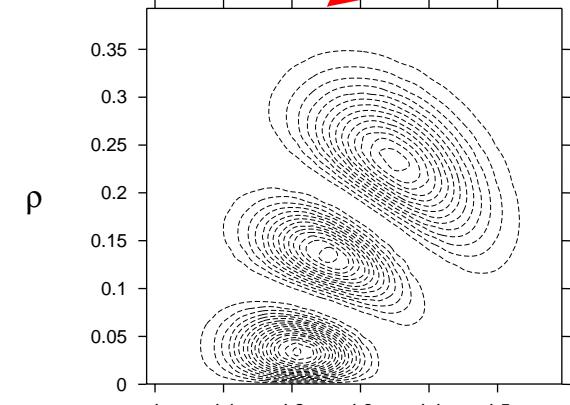
Fermi triad $\{(2,0^0,0)/(1,2^0,0)/(0,4^0,0)\}$



s



s

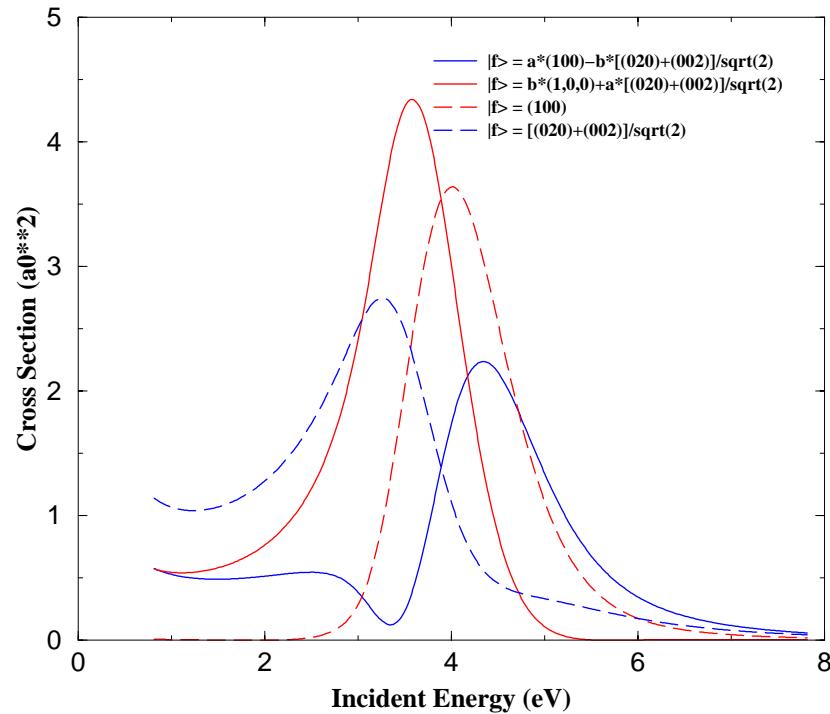


s

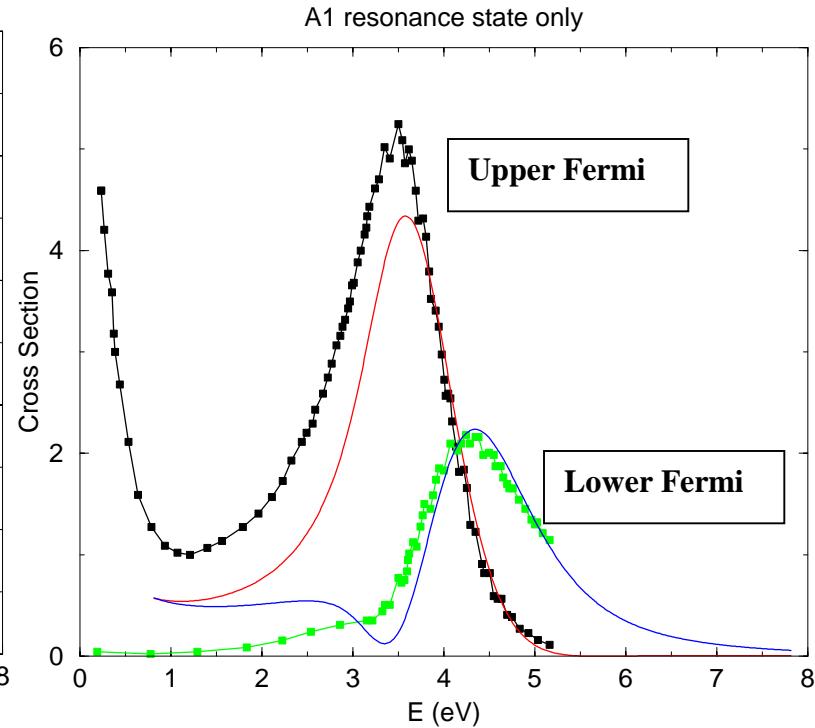
Suppose we use only the 2A_1 component of the resonance but include both stretch and bend?

Single Resonance Model – No “Boomerang structure” at all!

Accurate Target Vibrational States are Critical



Excitation of First Fermi Dyad



Multiple Resonances and Renner-Teller Coupling

Upon bending the $^2\Pi_u$ state splits into two resonances, 2A_1 and 2B_1 .

- The Born Oppenheimer approximation breaks down and these two states are coupled by an effect first characterized by Renner and Teller in 1934.

Normal Coordinates for CO₂

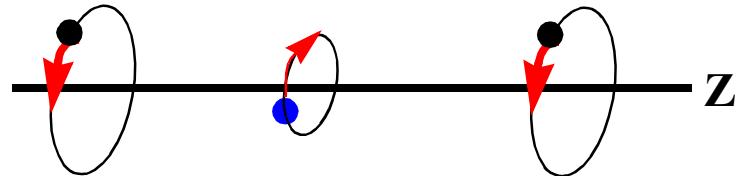
R = CO bond length

Θ = bend angle of CO from linear

$s = 2R \cos(\Theta)$ - Symmetric Stretch

$\rho = R^2 \sin^2(\Theta) / (1 + m_C / (2m_O))^2$ - bend

Degenerate Bending Modes



Degenerate bending modes can combine to give an angular momentum around the figure axis

Nuclear angular momentum K and electronic orbital angular momentum L give total angular momentum around the molecular axis $J_z = K_z + L_z$ resulting in “Renner-Teller” coupling proportional to $J_z L_z / \rho^2$

Coupled Boomerang Equations - Wave Packets on Both Surfaces

Scattering Amplitude:

$$T_{i,f}^{\alpha, \beta} = \frac{1}{i} \int_0^{\infty} e^{iEt} \langle \vec{X}_f, \beta | e^{-iHt} | \vec{X}_i, \beta \rangle dt$$

Two-state Hamiltonian:

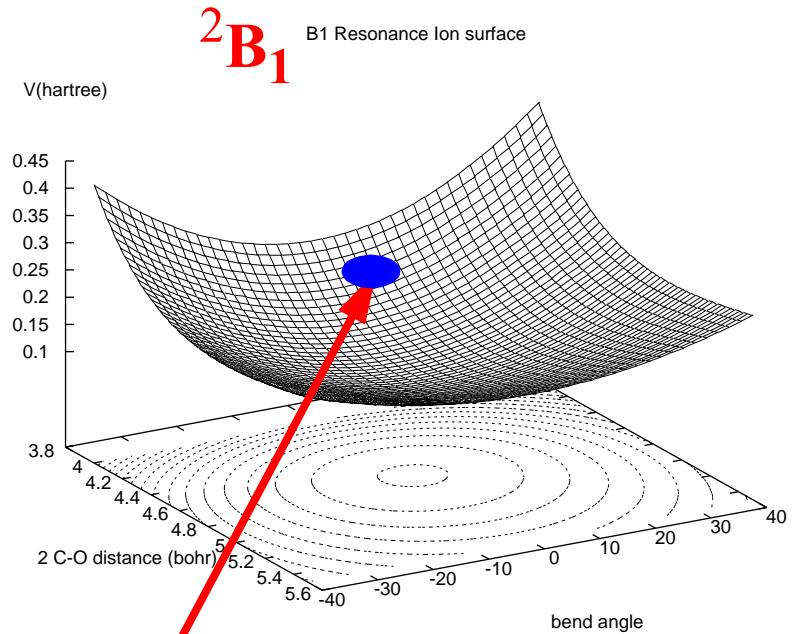
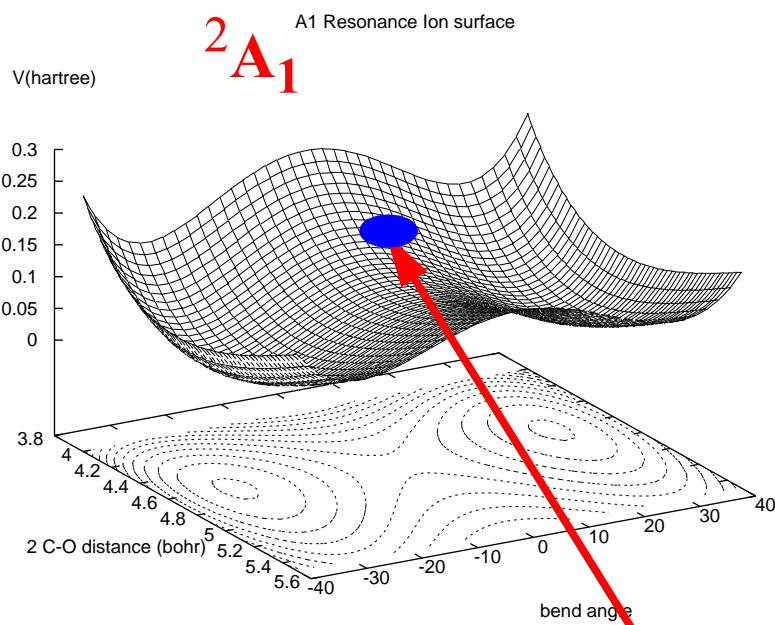
$$H = \begin{bmatrix} -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial s^2} - \frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial \rho^2} + \frac{\hbar^2}{2\rho^2} \left(J^2 + \frac{3}{4} \right) + V_{A_1}(s, \rho) & i \frac{\hbar^2}{\rho^2} J \\ -i \frac{\hbar^2}{\rho^2} J & -\frac{\hbar^2}{2\mu_1} \frac{\partial^2}{\partial s^2} - \frac{\hbar^2}{2\mu_2} \frac{\partial^2}{\partial \rho^2} + \frac{\hbar^2}{2\rho^2} \left(J^2 + \frac{3}{4} \right) + V_{B_1}(s, \rho) \end{bmatrix}$$

Initial and final wave packets begin on one surface or the other

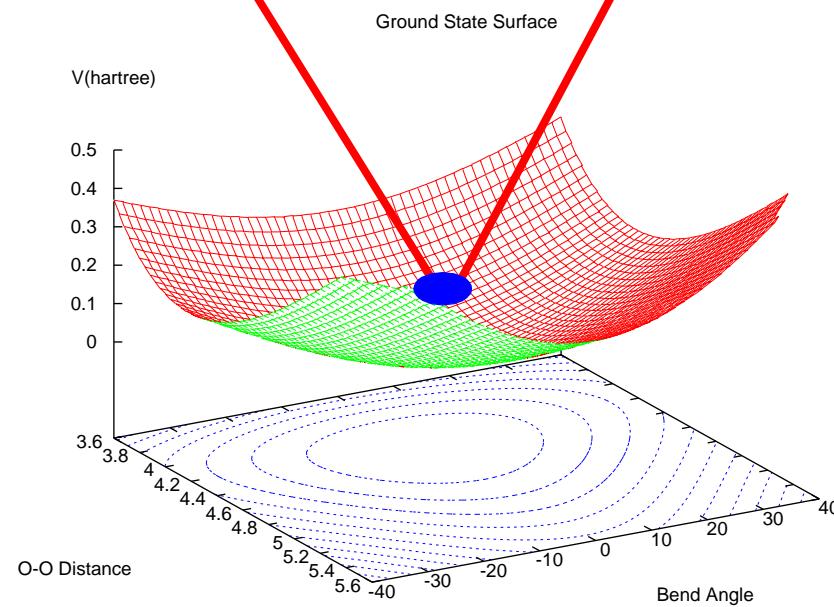
$$\vec{X}_{n,\alpha}(s, \rho) = \begin{pmatrix} \delta_{1\alpha} \left(\frac{\Gamma_1(s, \rho)}{2\pi} \right)^{1/2} \chi_n(s, \rho) \\ \delta_{2\alpha} \left(\frac{\Gamma_2(s, \rho)}{2\pi} \right)^{1/2} \chi_n(s, \rho) \end{pmatrix}$$

All four possibilities for beginning and ending surfaces contribute to cross section

$$\sigma_{f,i}(E) = \frac{4\pi^3}{k^2} (|T_{f,i}^{A,A}|^2 + |T_{f,i}^{A,B}|^2 + |T_{f,i}^{B,A}|^2 + |T_{f,i}^{B,B}|^2)$$



Multiple Resonance “Boomerang” approximation



Time : 1.000

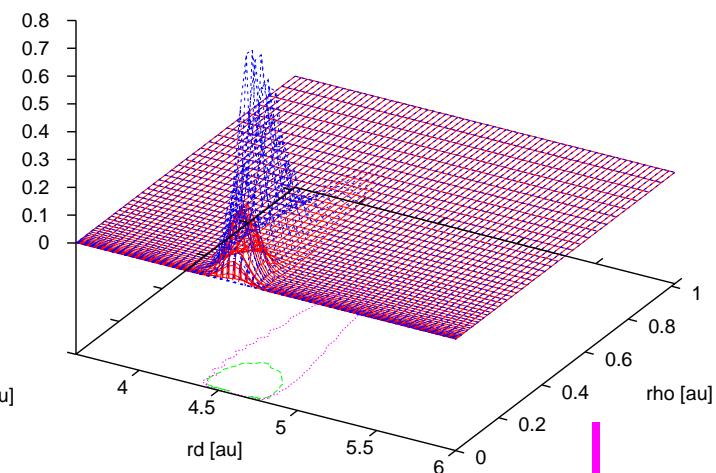
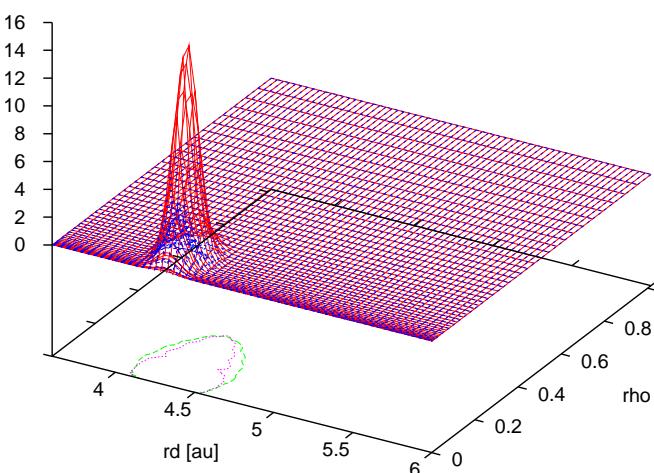
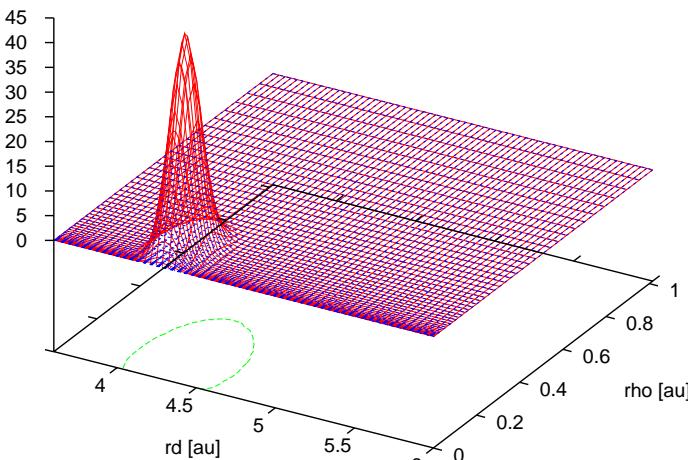
Time : 5.000

Density

Start on 2A_1

Density

Density



Time : 25.000

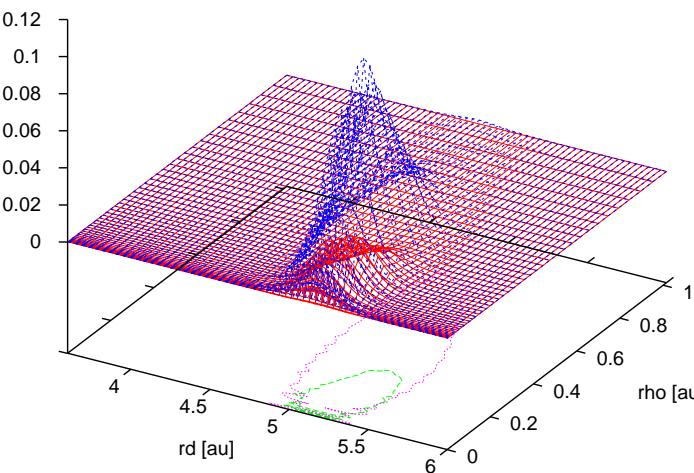
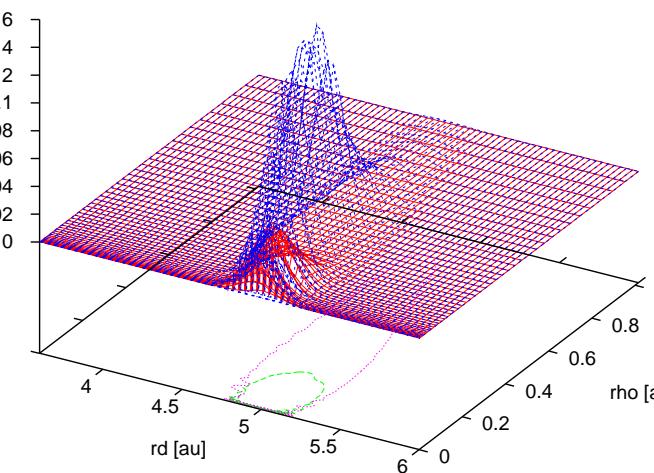
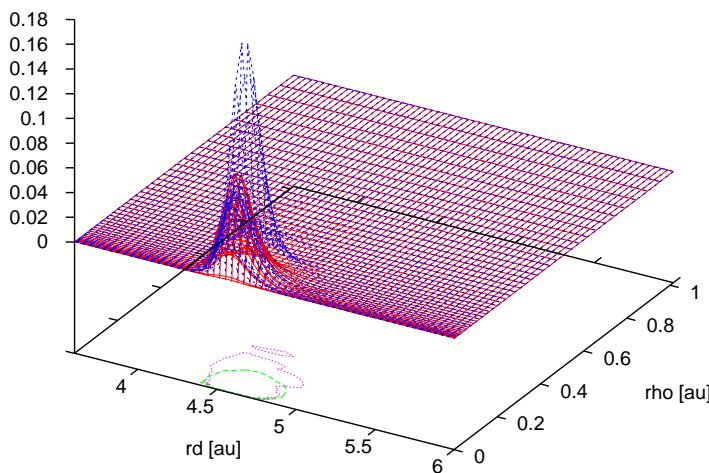
Time : 10.000

Time : 15.000

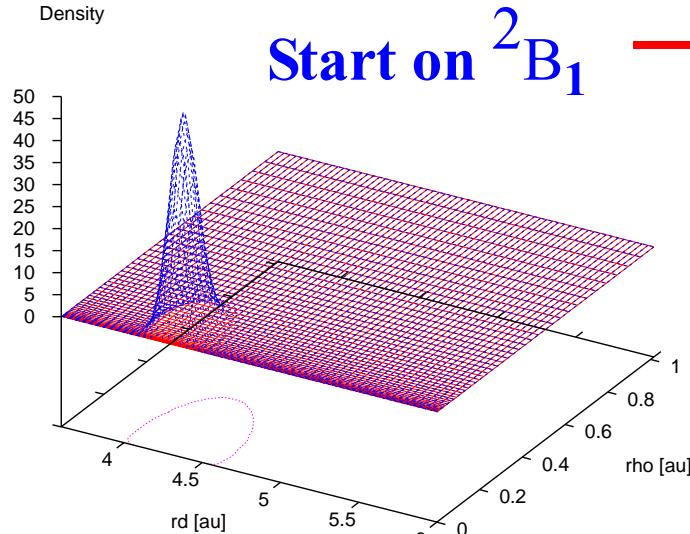
Density

Density

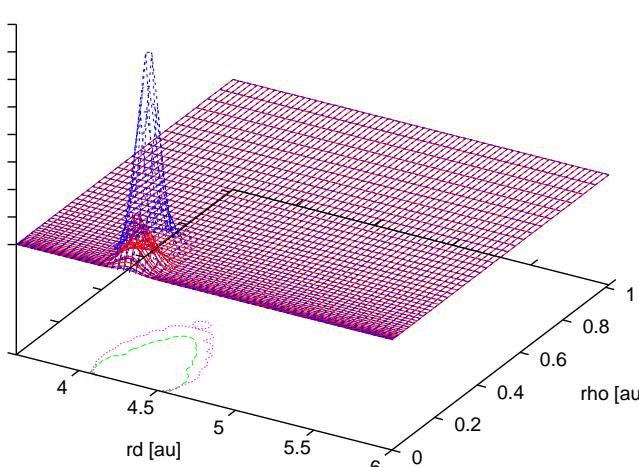
Density



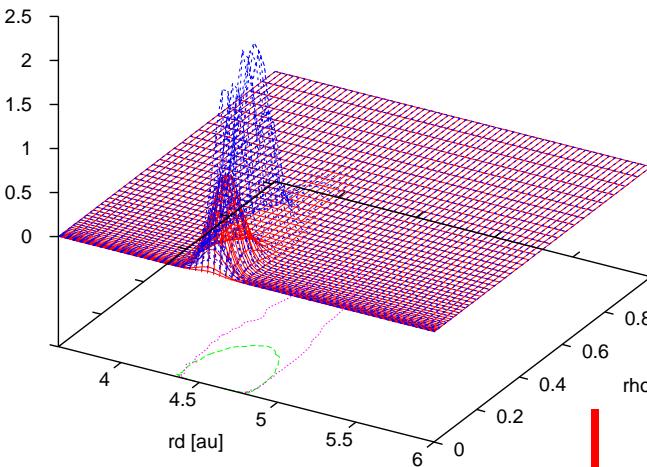
Density



Density

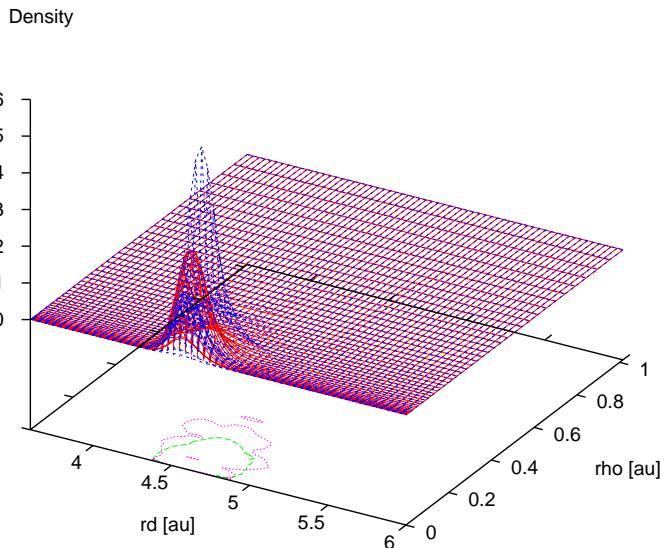


Density



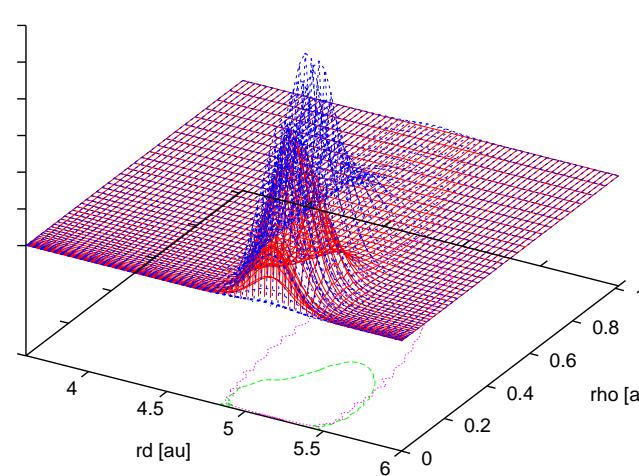
Time : 25.000

Density



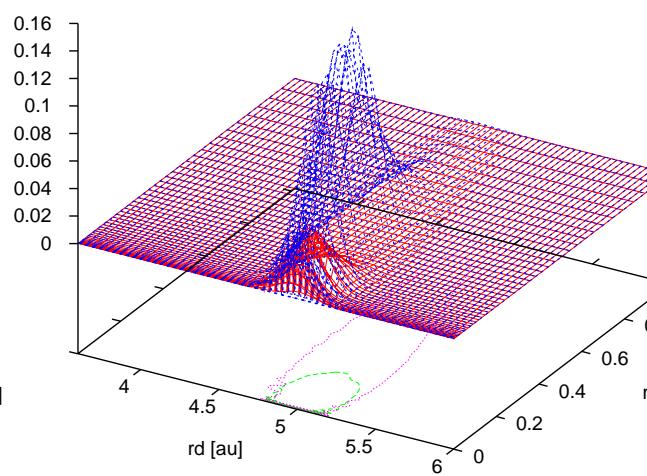
Time : 15.000

Density



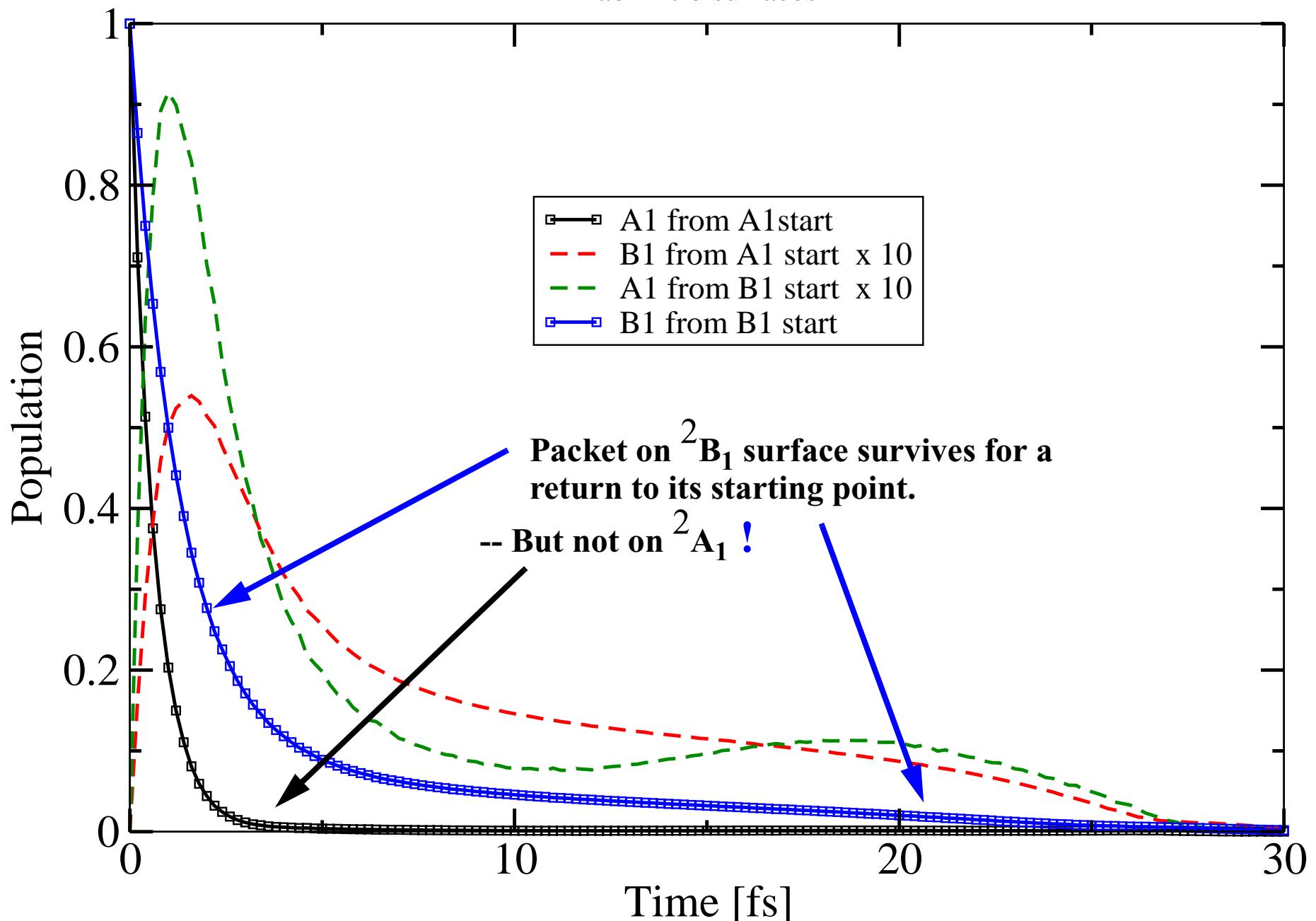
Time : 10.000

Density



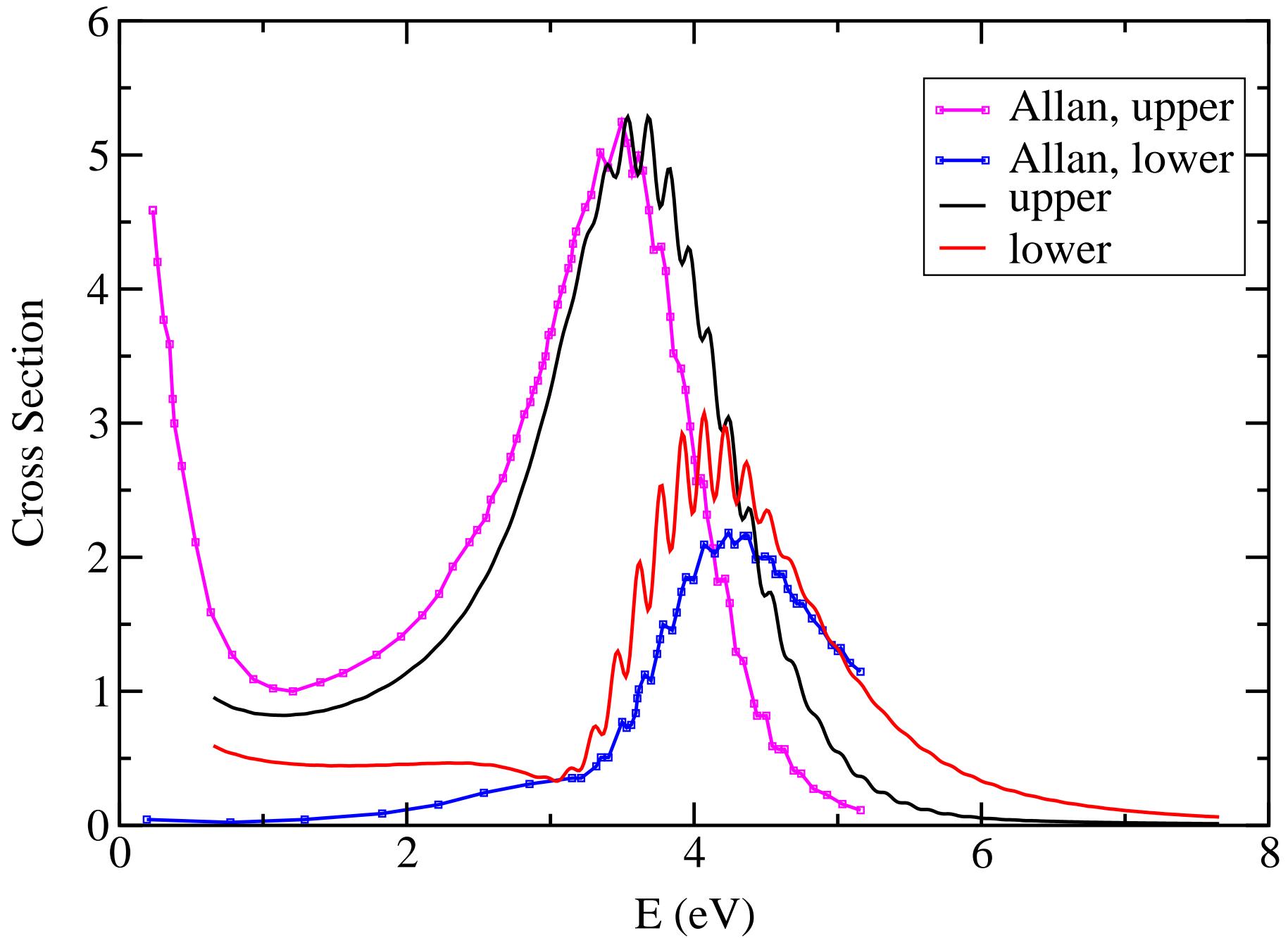
Electronic State Populations

ab initio surfaces



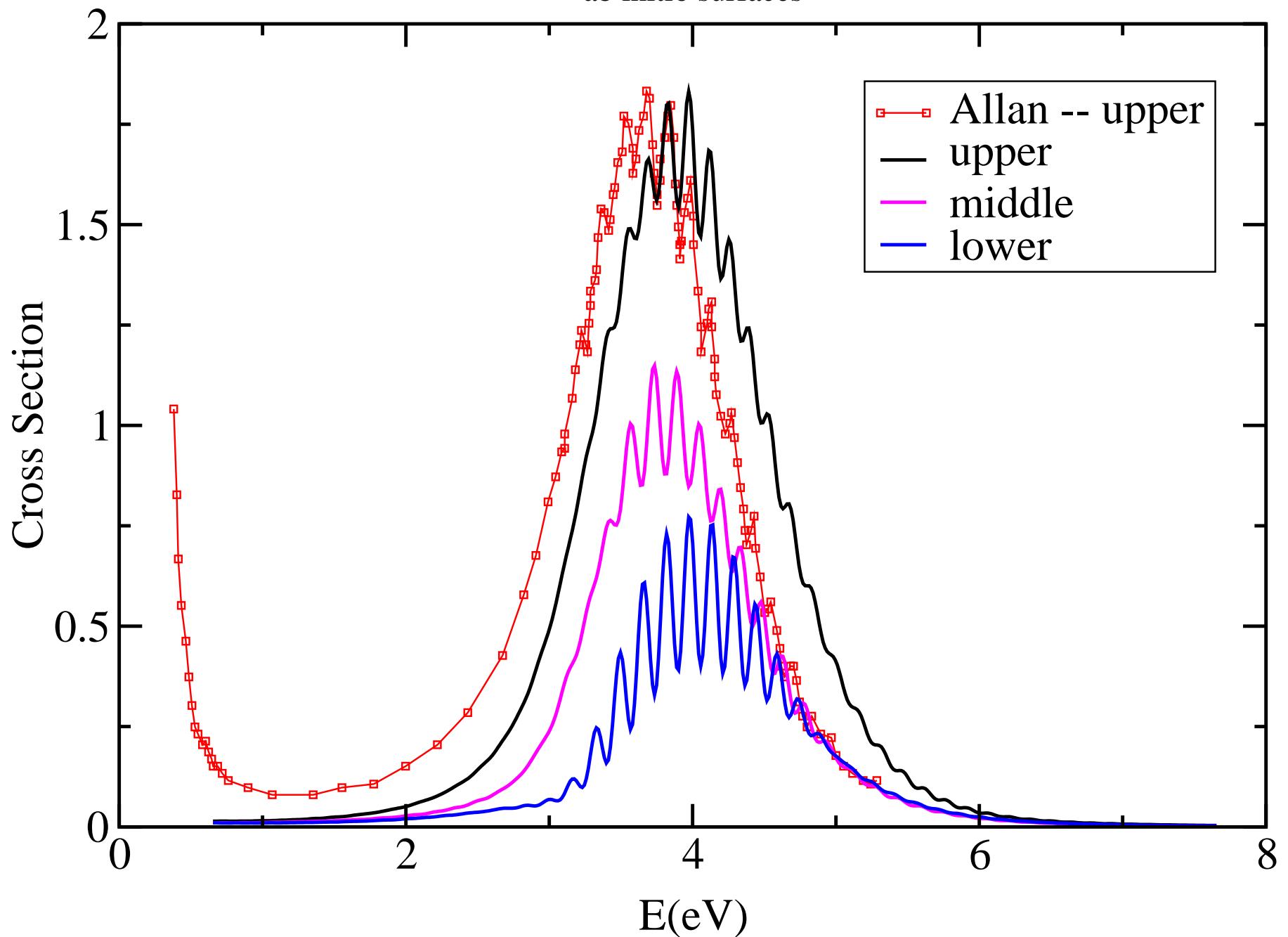
Excitation of First Fermi Dyad

Fully ab initio surfaces



Excitation of lowest Fermi Triad

ab initio surfaces



Differential Cross Sections in the Boomerang Model

- Assume angular dependence of scattered electron for each resonance state is given by a single partial wave *in the body-frame* of the molecule:

$$^2A_1 \rightarrow Y_y^{body}(\hat{\mathbf{k}}) = \frac{i}{\sqrt{2}} (Y_{1,-1}^{body}(\hat{\mathbf{k}}) + Y_{1,1}^{body}(\hat{\mathbf{k}}))$$

$$^2B_1 \rightarrow Y_x^{body}(\hat{\mathbf{k}}) = \frac{1}{\sqrt{2}} (Y_{1,-1}^{body}(\hat{\mathbf{k}}) - Y_{1,1}^{body}(\hat{\mathbf{k}}))$$

- The physical cross section is obtained by averaging over all orientations of the molecule with respect to a set of axes fixed *in the laboratory frame*. Transformations between frames are made using Wigner rotation matrices:

$$Y_{l,m}^{body}(\hat{\mathbf{k}}) = \sum_{\mu} Y_{l,\mu}^{lab}(\hat{\mathbf{k}}) D_{\mu,m}^l(\omega)$$

- The result (after much algebra!) is:

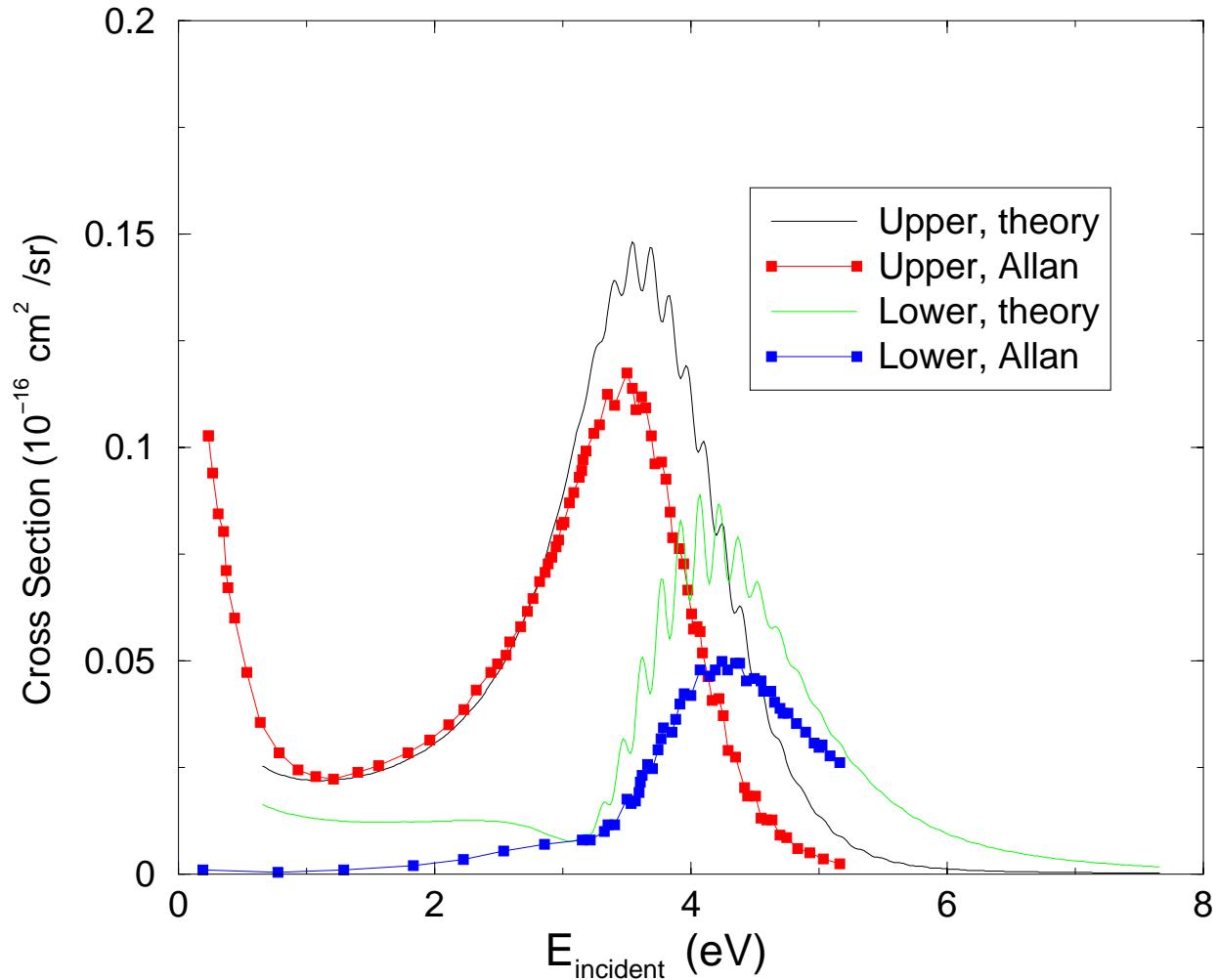
$$\frac{d\sigma}{d\Omega}(E) = \frac{3\pi^2}{20k^2} \left[(7 + \cos(2\theta))(|\tau_{1,1}|^2 + |\tau_{-1,-1}|^2 + |\tau_{1,-1}|^2 + |\tau_{-1,1}|^2) + (1 + 3\cos(2\theta))4 \operatorname{Re}(\tau_{1,1}^* \tau_{-1,-1}) \right]$$

$$\boldsymbol{\tau} = \mathbf{M}^t \mathbf{T} \mathbf{M}, \quad \mathbf{T} = \begin{pmatrix} T_{B,B} & T_{B,A} \\ T_{A,B} & T_{A,A} \end{pmatrix}, \quad \mathbf{M} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 & -1 \\ i & i \end{pmatrix}$$

Interference between resonances

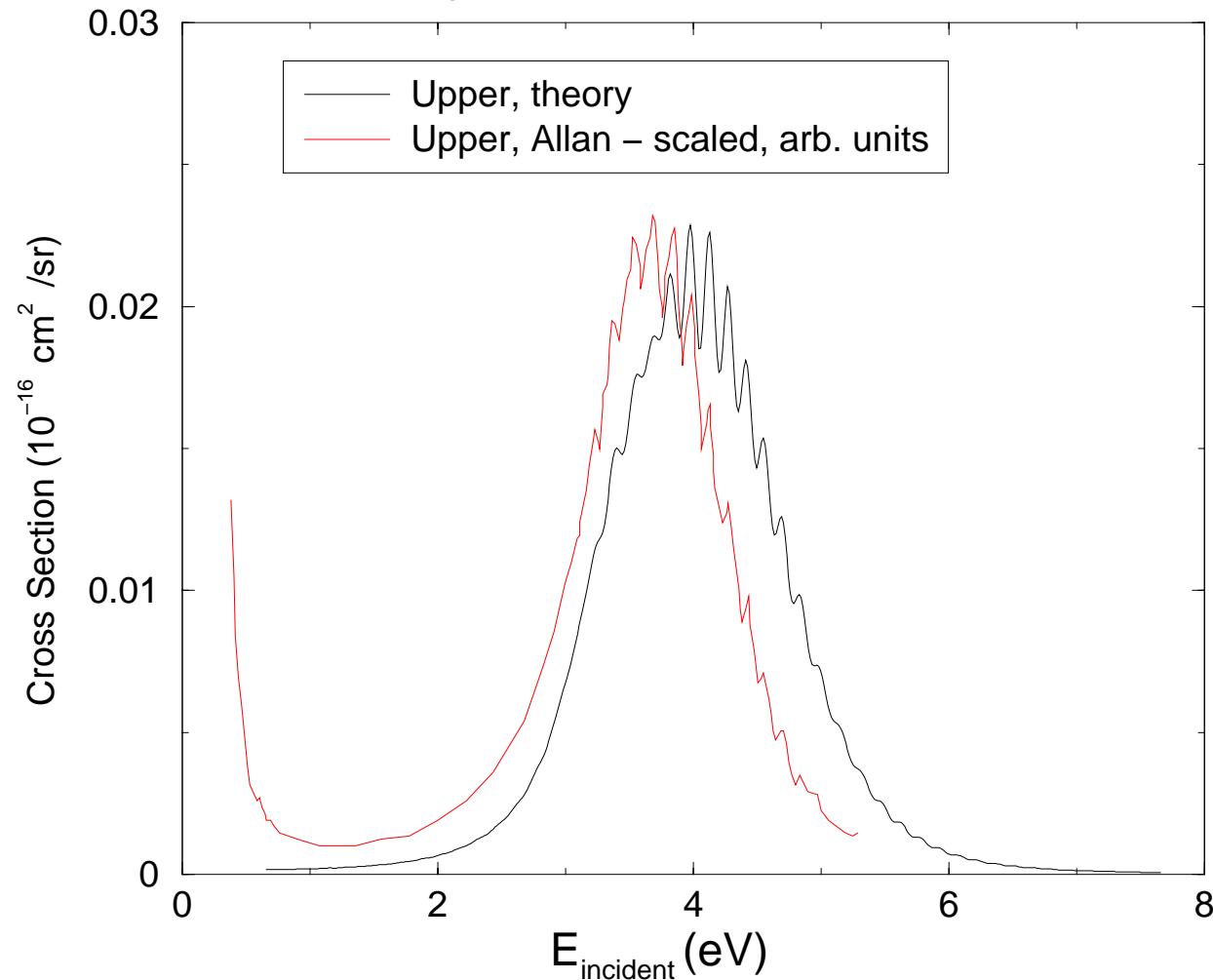
Absolute Differential Cross Sections 135^0

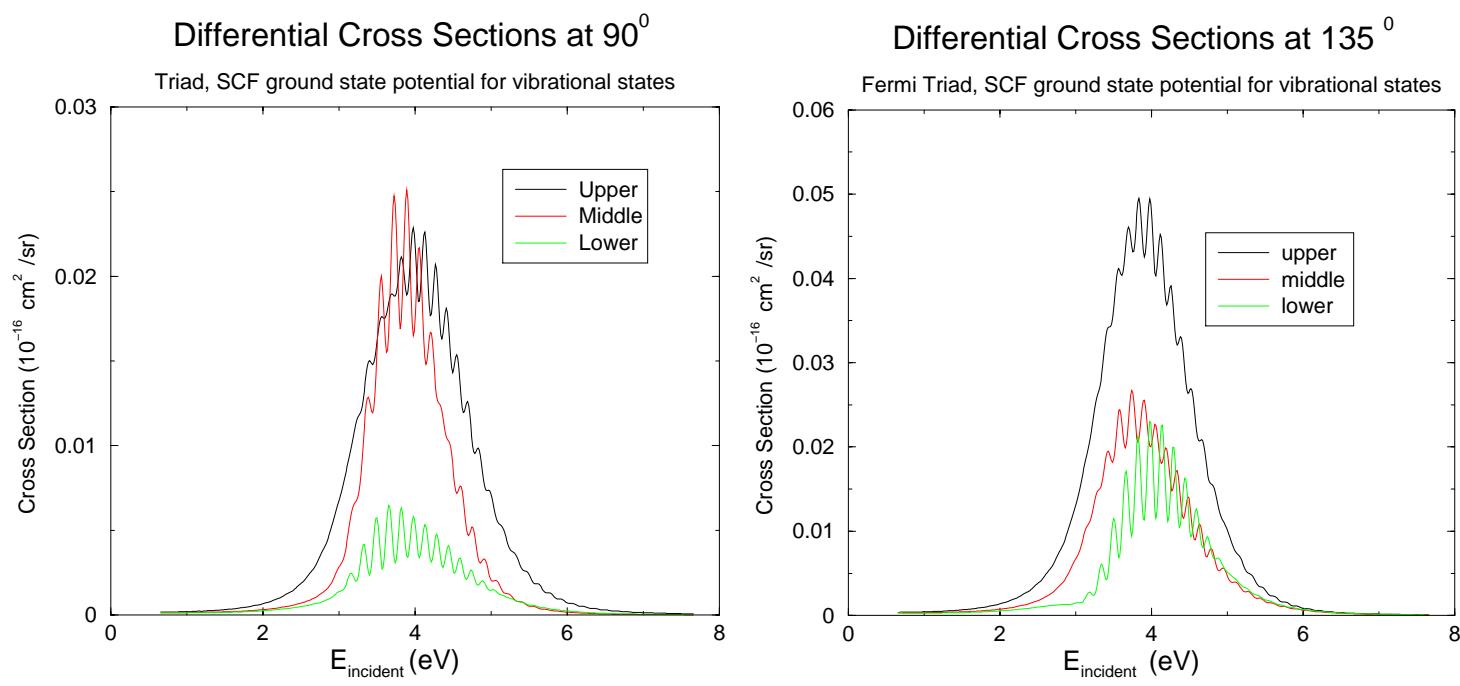
Fermi Dyad, SCF ground state potential for vibrational states



Differential Cross Sections at 90^0

Triad, SCF ground state potential for vibrational states



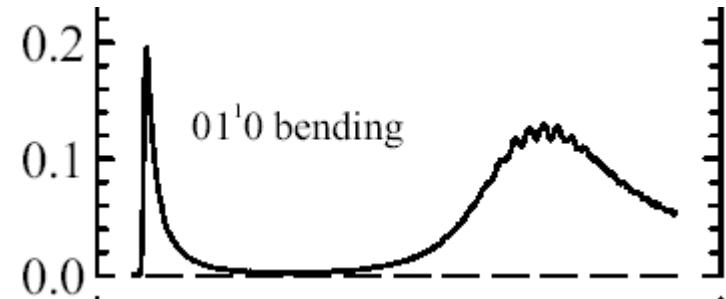


Some of what we have learned about electron-CO₂ collisions

- The resonance structure is an intrinsically polyatomic effect -- 1D models cannot account for it. The physical vibrational states of CO₂ are Fermi polyads that mix the bending and symmetric stretching modes.
- Motion on the A₁ surface alone cannot account for the resonance interference (“Boomerang”) structure in the cross sections.
- Renner-Teller coupling of ²A₁ and ²B₁ resonance states is necessary to describe the nuclear dynamics during resonant collisions.

Some of what have not learned

- The mechanism of resonance enhancement of the odd bending transitions -- like $(0,0,0) - (0,1,0)$. They are forbidden in the Boomerang model.



- Where the structure comes from in the threshold peaks

